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Abstract

Novel glasses in GeS_2-Sb_2S_3-AgI system have been prepared by melt-quenching method. A large glass-forming region was found in the novel system, in which almost 60mol% AgI has been incorporated. The basic physiochemical properties of glass samples were investigated. With the addition of AgI, red shift of short-wavelength absorption edge indicates and distinct drop of the glass transition temperature (T_g) were observed. In addition, a high Ag^+ ion conductivity of 6.37×10^{-4}S/cm at room temperature can be obtained in 55($0.6GeS_2$-$0.4Sb_2S_3$)-45AgI sample, indicating that these glasses have potential application as amorphous solid electrolytes.

Keywords: Amorphous materials, Electrical properties, Optical materials and properties.

1. Introduction

For several decades, chalcogenide glasses have attracted much attention due to their interesting properties: excellent IR transmittance, low phonon energy, high nonlinear refractive index, and good glass-forming abilities. Therefore, these materials present great potential for infrared optics applications

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such as thermal imaging, laser power delivering, and ultrafast all optical switching [1-5]. Among numerous glasses, Ge-Sb-S has been well studied and has been shown to possess good thermal stability and high nonlinear optical properties.[6-8] Moreover, the large glass-forming region and the compositional dependencies of various properties make it possible to tailoring material for different applications. Previous research revealed that adding AgI into sulphide glass can greatly improve the nonlinear optical properties.[9] And the addition of haloid atom, iodine, would improve the glass-forming ability. In addition, superionic conducting chalcogenide glasses containing Ag ions have potential application in solid-state batteries.[10-12] Therefore, we choose GeS_2-Sb_2S_3-AgI glasses which was not investigated before as research subjects.

In this paper, we synthesized chalcohalide glasses in GeS_2-Sb_2S_3-AgI system and investigated their glass-forming ability, thermal, optical, and physicochemical properties.

2. Experimental

Homogeneous GeS_2-Sb_2S_3-AgI glasses were obtained by melt-quenching method. High purity raw materials Ge, Sb, S (5N) and AgI (3N) were weighed in a glove box and mixed together. The mixtures were placed into pre-cleaned quartz ampoules and sealed under vacuum (~10^{-3}Pa). Then, the ampoules were melted at 950^{o}C for 12h in a rocking furnace and quenched in ice water to obtain bulk glasses. Subsequently, the glass samples were annealed at the temperature of T_g - 20^{o}C for 3h to remove inner constraints. Then the glass rods were cut and polished into disks of 10mm in diameter and 1mm in thickness.

Amorphous characteristics of the samples were confirmed by X-ray diffraction (Bruker D2 phaser, λ=0.15406 nm, 30 kv, 10 mA, Cu$K\alpha$). Densities were measured in de-ionized water based on the

Archimedes principle. Vickers hardness values were obtained by Vickers microindenter (Everone MH-3, Everone Enterprises. Ltd., China) with a charge of 100g for 5s. The glass transition temperature (T_g) and the onset of crystallization temperature (T_x) were determined by DSC (TA Instruments Q2000, New Castle, DE) at a heating rate of 10 ^{o}C/min. The transmission spectra were recorded with a UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950, Waltham, MA) and FTIR spectrometer (Nicolet 381, USA). In addition, the conductivities were calculated from impendence spectra which were carried out using an impedance analyzer (Agilent 4294A, USA).

3. Results and Discussion

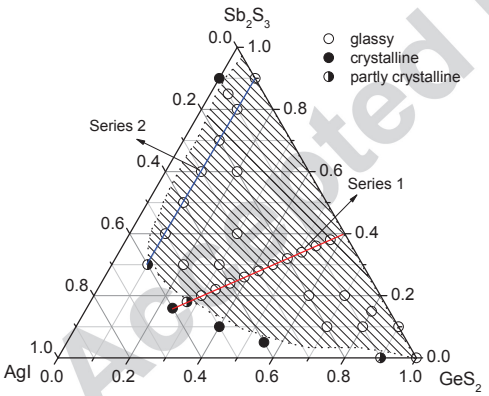

Fig.1

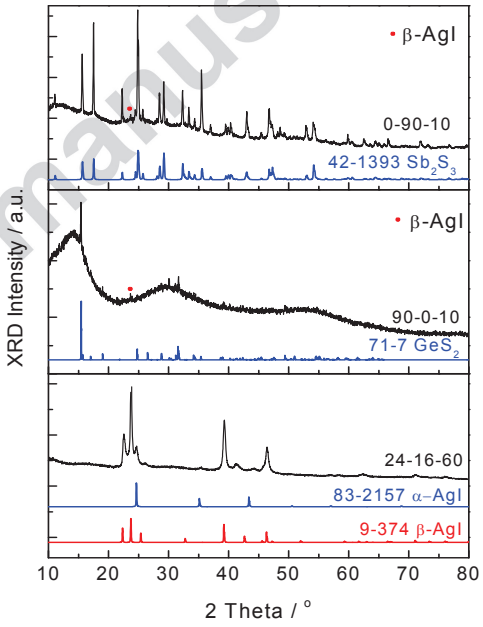

Fig. 2

A relatively wide glass-forming region was determined in the case of quenching 10g melts in water and shown in **Fig. 1**. It can be seen that the glass forming region is very large, and AgI can be largely incorporated into the GeS_2-Sb_2S_3 glasses. In the pseudo-ternary system, the amount of dissolved AgI can be reach to ~55mol% when the ratio of GeS_2 to Sb_2S_3 is 6/4 (series 1). With a constant of 10mol% GeS_2

content (series 2), the glass-forming region reaches to ~60mol% amount of AgI. The large glass forming region is important because the large amount of AgI can enhances ionic conductivity and provides super-ionic glasses. **Fig. 2** shows the XRD patterns of some crystallized samples. Here the sample with the composition of $x$$GeS_2$-$y$$Sb_2S_3$-$z$AgI is named as x-y-z. It is obvious that no glass is obtained along the Sb_2S_3-AgI side. In the GeS_2-AgI system, sample with 10% AgI has GeS_2 and β-AgI crystalline separate out. In the pseudo-ternary system, along the series 1, sample with 60% AgI (24-16-60) has the separation of crystalline α-AgI and β-AgI.

Table 1 Density, hardness and characteristic temperature of the samples.

	Compositions	Density, ρ ($\pm$0.002g/cm^3)	Hardness, H_v ($\pm$2kg/mm^2)	T_g ($\pm$1°C)	T_x ($\pm$1°C)	ΔT (T_x-T_g)
Series 1	90(0.6GeS_2·0.4Sb_2S_3)-10AgI	3.749	160	231	399	168
	80(0.6GeS_2·0.4Sb_2S_3)-20AgI	3.952	142	213	400	187
	70(0.6GeS_2·0.4Sb_2S_3)-30AgI	4.192	130	187	401	214
	60(0.6GeS_2·0.4Sb_2S_3)-40AgI	4.441	114	182	402	220
	55(0.6GeS_2·0.4Sb_2S_3)-45AgI	4.481	104	155	402	247
Series 2	10GeS_2-80Sb_2S_3-10AgI	4.245	143	215	286	71
	10GeS_2-70Sb_2S_3-20AgI	4.346	141	203	298	95
	10GeS_2-60Sb_2S_3-30AgI	4.397	136	187	305	118
	10GeS_2-50Sb_2S_3-40AgI	4.616	120	178	305	127
	10GeS_2-40Sb_2S_3-50AgI	4.762	107	162	313	151

The detailed parameters of samples are provided in **Table 1**. It is obviously that, with increasing contents of AgI, the density increases and the hardness decreases. The evolution of density is easy to understand because of the heavy mass of AgI. The variation of hardness is also due to the addition of iodine atoms. As a non-bridging atom, iodine plays the role as the glass network terminator and breaks M-S-M (M=Ge or Sb) bonds to form M-I bonds. Thus, the addition of AgI decreases the dimensionality of structural network and makes the network more opened, and consequently resulting in the decrease of hardness. Previous research found that the T_g have an intimate relationship with the crosslink density and

the network connectivity of the glasses.[13] As discussed above, iodine atom is a glass network terminator, and the addition of iodine will induce the descending of network connectivity. Thus, the value of T_g will decrease with the addition of AgI gradually.

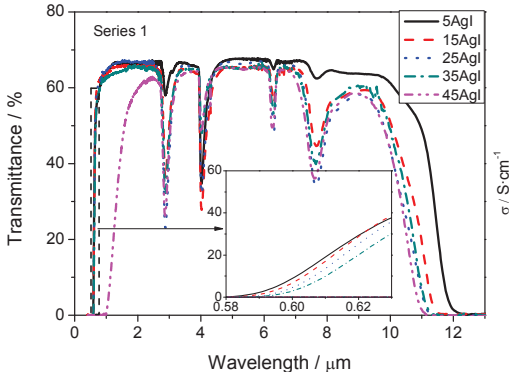

Fig.3

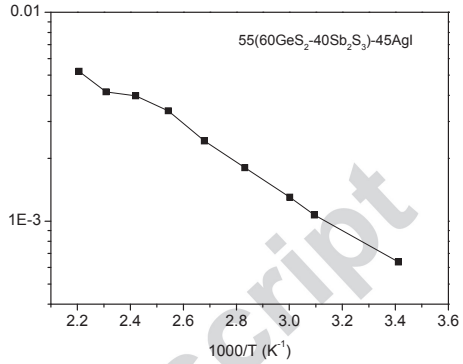

Fig. 4

Fig. 3 shows the Vis-IR transmission spectra of GeS_2-Sb_2S_3-AgI glasses. Most of these glasses have good transparency in IR region, but the transmission region becomes narrow with the addition of AgI. According to previous researches[14, 15], the addition of halides in chalcogenide glass would usually induce the blue shift of the cut-off edge of short wavelength (λ_{vis}) due to the lower polarizability of haloid ions compared with S^{2-} ions. Herein, on the contrary, λ_{vis} shifts toward the long wavelength with the addition of AgI. This is probably because of the high polarizability of Ag^+ ions. Furthermore, the absorption bands at 2.9μm, 6.3μm, and 7.7μm can be attributed to the -OH, H_2O, and -S-O-, respectively. These IR impurity absorption bands are enhanced with the addition of AgI because of its hygroscopic property.

As discussed above, the large amount of AgI may provide superionic glasses. To identify whether these glasses have superionic conducting characteristic, we employed impendence spectra to calculate the conductivity. The total conductivity contains ionic and electronic contribution. Here the electronic conductivity is negligibly small compared to the ionic one. The calculated results were plotted in **Fig. 4**.

The results showed that the conductivity at room temperature for 55($0.6GeS_2$-$0.4Sb_2S_3$)-45AgI is 6.37×10^{-4}S/cm. The high conductivity can be attributed to the mobile Ag ions in glass matrix.

4. Conclusion

In this work, we prepared GeS_2-Sb_2S_3-AgI chalcogenide glasses and determined the glass-forming region. Up to almost 60mol% AgI can be dissolved in this glass system. The glasses have excellent IR transmittance which makes them good materials for application in IR optics. In addition, the high Ag^+ ion conductivity of 6.37×10^{-4}S/cm at room temperature can be obtained for 55($0.6GeS_2$-$0.4Sb_2S_3$)-45AgI sample. This results indicating that this glass system has a potential application in amorphous solid electrolytes.

Acknowledgements

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Figure captions

Fig. 1 Glass-forming region of GeS_2-Sb_2S_3-AgI system.

Fig. 2 XRD patterns of some crystallized samples and the JCPDF cards of no. 83-2157 α-AgI and no.

9-374 β-AgI.

Fig. 3 Vis-IR transmission spectra of glass samples in series 1.

Fig. 4 Temperature dependence of the conductivity for 55($0.6GeS_2$-$0.4Sb_2S_3$)-45AgI glass.

Highlights

1. The first research about the novel GeS_2-Sb_2S_3-AgI system.

2. The glass-forming region is very large in this system, and large amount of AgI can dissolved in this system.

3. The ionic conductivity at room temperature of $55(60GeS_2\text{-}40Sb_2S_3)$-45AgI can reach to 6.37×10^{-4}S/cm, indicating that this glass system has a potential application in amorphous solid electrolytes.